FOOTWEAR-COMPOUNDS FROM DERIVATIZED STAR-BLOCK COPOLYMERS

BACKGROUND OF THE INVENTION

The present invention relates to star-block polymers and copolymers of monovinylaromatic compounds and conjugated dienes having functional groups associated with the nucleus of the copolymers. More specifically, the invention relates to footwear compounds comprising these resinous star-block copolymers.

Highly branched block copolymers, sometimes called star-block copolymers, are known in the art of anionic polymerization. These star-block copolymers are prepared by first forming linear block polymers having an active lithium atom on one end of the polymer chain. These active, linear polymer chains are then coupled by the addition of a polyfunctional compound having at least three reactive sites capable of reacting with the carbon to lithium bond on the polymer chains to add the polymer chain onto the functional groups of the compound. In the case where the polyfunctional compound is divinylbenzene, the coupling reaction results in a star-block having a cluster of living anionic species at the nucleus of the star. It is at this point that the reactive star anions are normally terminated by reaction with proton active reagents, such as alcohols, to yield the final polymer.

Zelinski, U.S. Pat. No. 3,280,084, polymerized butadiene with butyllithium initiator to form B-Li blocks (where B is polybutadiene) which when coupled with 0.02 to 1 part by weight per 100 parts of monomers of divinylbenzene gave star-block copolymers having polydivinylbenzene nuclei and several identical arms of polybutadiene branching therefrom. The arms can also be either random or block copolymers of styrene and butadiene (from A-B-Li blocks, where A is polystyrene segment) where the diene is the major component.

Farrar, U.S. Pat. No. 3,644,322, teaches to make star-block copolymers having several arms wherein half of the arms are grown out from the nucleus and then terminated with carbon dioxide or epoxides to form polar functional groups at the outer extremities of these arms.

Fletcher, U.S. Pat. No. 3,755,283, prepares hydroxyphenyl terminated star-block copolymers by using lithium p-lithiophenoxide as an initator of linear chains, which chains are then coupled with polyfunctional coupling agents to form the star-block copolymers having the functional groups distant from the nucleus.

Milkovich et al., U.S. Pat. No. 3,786,116, teaches the end capping of linear block copolymers by reacting the carbon-to-lithium ends with various functional groups-producing terminating agents. These agents, primarily produced by reacting halogen-containing compounds having a polymerizable moiety such as an olefinic group or an epoxy group, produced polymerizable block copolymers named macromonomers.

Fetters et al., U.S. Pat. No. 3,985,830, discloses a product having a nucleus of more than one molecule of m-divinylbenzene and at least three polymeric arms, each being a block copolymer of conjugated diene and monovinyl aromatic monomers wherein said conjugated diene block is linked to said nucleus.

Crossland et al., U.S. Pat. No. 4,010,226, teaches to form star-block copolymers using divinylbenzene as coupling agent, growing new arms from this star-block copolymers, which arms are 5000 to 1,000,000 molecular weight and then capping these longer arms at the extremities away from the nucleus with various reagents which react with the carbon-to-lithium bonds.

Tung et al., U.S. Pat. No. 4,169,115, teaches to form linear block copolymers which are then terminated by adding an episulfide. The terminated copolymer is then copolymerized with styrene by a free-radical initator to form block copolymers.

Bi et al., U.S. Pat. No. 4,180,530, teaches to form star-block copolymers having 60–95% by weight of a monovinyl aromatic compound and 5–40% by weight of a conjugated diene and having general formula $(A\text{-}A'/B\text{-}B')_m X\text{-}B'(B/A')_n$, where A is a block of vinyl aromatic compound, A'/B or B/A' is a block of random copolymer of the vinyl aromatic compound and the conjugated diene, B' is a block of conjugated diene monomer, m and n are integers whose sum is between 3 and 20, and X is the radical of a polyfunctional coupling agent forming the nucleus of the bimodal star-block copolymer.

SUMMARY OF THE INVENTION

It has now been found that star-block copolymers formed with polyvinyl aromatic compounds as the coupling agent can be improved by reacting the star-block copolymer, prior to termination of the living anions formed at the nucleus, with a derivatization agent which reacts with the central carbon-to-lithium bonds to form active polar functional groups on the nucleus of the star-block copolymers. These derivatized copolymers can be formulated into shoesole compounds which have better processability than compounds made with star-block copolymers not having functional groups on the nucleus.

DETAILED DESCRIPTION OF THE INVENTION

The polymers of this invention are star-block copolymers of from 10 to 55% by weight of a monovinyl aromatic compound and 45 to 90% by weight of a conjugated diene of 4 to 8 carbon atoms and said star-block copolymers having at least three arms connected to a polyvinyl aromatic compound nucleus and up to the same number of polar functional groups attached to said nucleus as there are arms attached thereto.

The polymers are prepared by polymerizing monovinyl aromatic compounds and/or conjugated dienes in an inert hydrocarbon solvent with a hydrocarbyllithium initiator and coupling the resulting block polymer or copolymer chains with polyvinyl aromatic compounds. At this point the living anionic chains transfer the active sites to the polyvinyl aromatic compound nucleus to form a cluster of living anionic species at the center of the star-block polymer. In the known process for preparing star-block polymers, these living anionic species are terminated with proton active substances, such as alcohols, to yield the protonated polymers. In the present invention, the living anionic species are reacted, prior to termination, with a derivatization agent to put polar functional groups on the nucleus of the star-block copolymers.

The structure of the arms of the star-block copolymers can be any of the known block structures made up of poly (vinyl aromatic compound) and/or poly (conjugated diene). Included in these structures are the homopolymer blocks, the true copolymer blocks, the random copolymer blocks, the tapered copolymers blocks and mixtures of these. The arms themselves of any one star-